

CLAIMS

5 1. A catalyst for addition polymerisation of olefinically unsaturated monomers comprising:

10 a) A first compound

MY

where: M is a transition metal in a low valency state or a transition metal in a low valency state co-ordinated to at least one co-ordinating non-charged ligand.

Y is a monovalent divalent or polyvalent counterion;

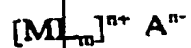
15 b) An initiator compound comprising a homolytically cleavable bond with a halogen atom; and

c) An organodiimine, where at least one of the nitrogens of the diimine is not part of an aromatic ring.

20 2. A catalyst for addition polymerisation of olefinically unsaturated

monomers comprising:

d) A first component of Formula



where:

M = a transition metal of low valency state

L = an organodiimine where at least one of the nitrogens of the diimine is not a part of an aromatic ring.

A = an anion

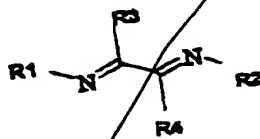
n = an integer of 1 to 3

m = an integer of 1 to 2, and

e) An initiator compound comprising a homolytically cleavable bond with a halogen atom.

2  
3. A catalyst according to ~~any previous claim~~ <sup>claim 1</sup> wherein the organodiimine is selected from:

a 1,4-diaza-1,3-butadiene

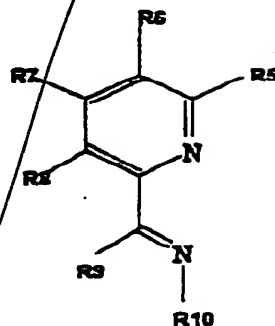


Formula 24

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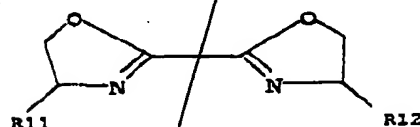
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46  
a 2-pyridine carbaldehyde imine



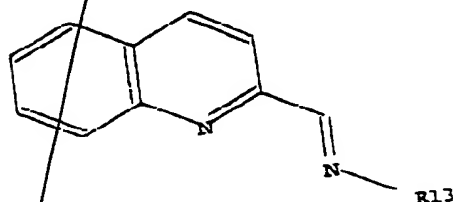
Formula 25

an oxazolidone



Formula 26

or a quinoline carbaldehyde



Formula 27

where:

R<sub>1</sub>, R<sub>2</sub>, R<sub>10</sub>, R<sub>11</sub>, R<sub>12</sub> and R<sub>13</sub> are independently selectable and may be selected from H, straight chain, branched chain or cyclic saturated alkyl, hydroxyalkyl, carboxyalkyl, aryl, CH<sub>2</sub> Ar (where Ar is aryl or substituted) or a halogen;

*SN  
B  
Cr*

$R_3$  to  $R_9$  are independently selectable and may be selected from H, straight chain, branched chain or cyclic alkyl, hydroxyalkyl, carboxyalkyl, aryl,  $\text{CH}_2$  Ar, a halogen,  $\text{OCH}_{2n+1}$  (where  $n$  is an integer of 1 to 20),  $\text{NO}_2$ , CN,  $\text{O} = \text{CR}$  (where  $R$  = alkyl, aryl, substituted aryl, benzyl  $\text{PhCH}_2$  or a substituted benzyl).

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*B*

*3* A catalyst according to claim *2* wherein  $R_1$  to  $R_{13}$  are selected from *the group consisting of:*  
 $C_1$  to  $C_{20}$  alkyl,  $C_1$  to  $C_{20}$  hydroxyalkyl,  $C_1$  to  $C_{20}$  carboxyalkyl, n-propylisopropyl, n-butyl, sec-butyl, tert-butyl, cyclohexyl, 2-ethylhexyl, octyldecyl *and* lauryl.

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*a*

*9* A catalyst according to claim *3* or claim *4*, wherein the organodiimine comprises a chiral centre.

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*claim 3*

*5* A catalyst according to ~~claims 3 to 5~~ wherein one or more adjacent  $R_1$  and  $R_3$ ,  $R_3$  and  $R_4$ ,  $R_4$  and  $R_2$ ,  $R_{10}$  and  $R_9$ ,  $R_8$  and  $R_9$ ,  $R_8$  and  $R_7$ ,  $R_7$  and  $R_6$ ,  $R_6$  and  $R_5$  groups are selected from *the group consisting of* alkyl, cycloalkenyl, polycycloalkyl, polycycloalkenyl *and* cyclicaryl, containing 5 to 8 carbon atoms.

20

48 *claim 1*

*B a*  
6. A catalyst according to ~~any previous claim~~ wherein M is selected from *the group consisting of* Cu(I), Fe(II), Co(II), Ru(II), Ni(II), Sm(II), Ag(I) and Yb(II).

*claim 1*

*AB5*  
7. A catalyst according to ~~any of claims 1 and 3 to 7~~, wherein Y is *the group consisting of* selected from Cl, Br, I, NO<sub>3</sub>, PF<sub>6</sub>, BF<sub>4</sub>, SO<sub>4</sub> and CF<sub>3</sub>, SO<sub>3</sub>, CN, SPh, SCN and SePh.

*claim 2*

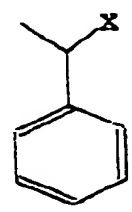
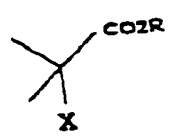
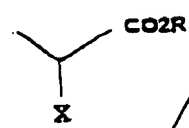
9. A catalyst according to ~~any of claims 2 to 7~~ wherein A is selected from Cl, Br, F, I, NO<sub>3</sub>, SO<sub>4</sub> and CuX<sub>2</sub> (where X is a halogen).

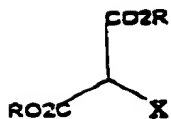
*claim 1*

8. A catalyst according to ~~any previous claim~~, wherein the initiator is selected from:

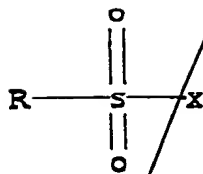
RX

Formula 2

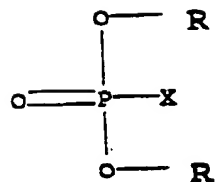




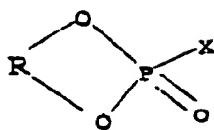
### Formula 6



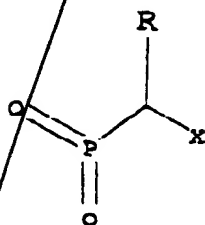
### Formula 7



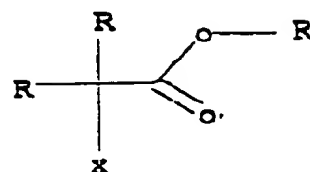
### Formula 8



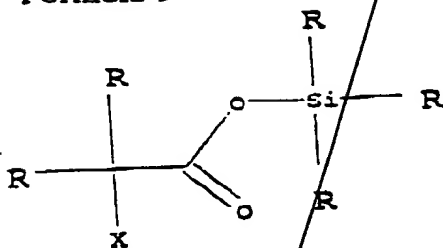
### Formula 9



### Formula 10



### Formula 11



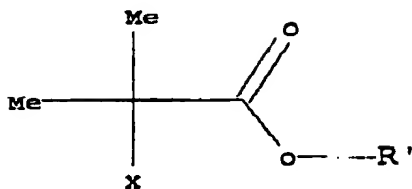
### Formula 12

Formula 12

where R is independently selectable and is selected from straight chain alkyl, branched chain alkyl, cyclic alkyl, hydrogen, substituted alkyl, hydroxyalkyl, carboxyalkyl, aryl and substituted aryl and substituted benzyl.

**X  $\neq$  a halide**

9  
11. A catalyst according to claim 10, wherein the initiator is



wherein  
where:

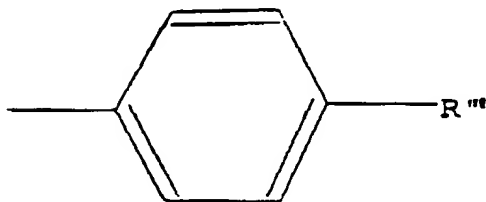
X = Br, I or Cl, preferably Br

R' = -H,

$-(CH_2)_pR''$ , where p is a whole number and R'' = H, OH,

NH<sub>2</sub>, SO<sub>3</sub>H, COOH, halide, COX, where X is Br, I or Cl,

or



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R''' = -COOH, -COX, where X is Br, I or Cl, -OH, -NH<sub>2</sub> or -SO<sub>3</sub>H.

10  
12. A catalyst according to claim 11 wherein (b) is 2-hydroxyethyl-2'-  
bromopropionate.

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13. The use of a catalyst according to ~~any previous claim~~ claim 1 in the

addition polymerisation of one or more olefinically saturated monomers.

<sup>12</sup>  
14. The use of a catalyst according to claim <sup>11</sup> 13 at a temperature between -20°C to 200°C.

<sup>13</sup>  
15. The use of a catalyst according to claim <sup>12</sup> 14 between 20°C and 130°C.

<sup>14</sup>  
16. The use of a catalyst according to <sup>claim 13</sup> ~~claims 13 to 15~~, wherein the olefinically saturated monomer is selected from methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), and other alkyl methacrylates; corresponding acrylates; also functionalised methacrylates and acrylates including glycidyl methacrylate, trimethoxysilyl propyl methacrylate, allyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, dialkylaminoalkyl methacrylates; fluoroalkyl (meth)acrylates: methacrylic acid, acrylic acid; fumaric acid (and esters), itaconic acid (and esters), maleic anhydride; styrene,  $\alpha$ -methyl styrene; vinyl halides such as vinyl chloride and vinyl fluoride; acrylonitrile, methacrylonitrile; vinylidene halides of formula  $\text{CH}_2 = \text{C}(\text{Hal})_2$  where each halogen is independently Cl or F; optionally substituted butadienes of the formula  $\text{CH}_2 = \text{C}(\text{R}^{14}) \text{C}(\text{R}^{15}) = \text{CH}_2$  where

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S  
N  
B4  
cont

a



$R^{15}$  is independently H, C1 to C10 alkyl, Cl, or F; sulphonic acids or derivatives thereof of formula  $CH_2 = CHSO_2OM$  wherein M is Na, K, Li,  $N(R^{16})_4$ ,  $R^{16}$ , or  $-(CH_2)_2-D$  where each  $R^{16}$  is independently H or Cl or C10 alkyl, D is  $CO_2Z$ , OH,  $N(R^{16})_2$ , or  $SO_2OZ$  and Z is H, Li, Na, K or  $N(R^{16})_4$ ; acrylamide or derivatives thereof of formula  $CH_2 = CHCON(R^{16})_2$ , and methacrylamide or derivatives thereof of formula  $CH_2 - C(CH_3)CON(R^{16})_2$ . Mixtures of such monomers may be used.

17. The use of a catalyst, as defined in claims 1 and 3 to 12, according to claims 13 to 16, wherein the ratio (c):(a) is 0.01 to 1000 and the ratio of (a):(b) is 0.0001 to 1000.

18. The use of a catalyst as defined in claims 2 to 12 according to claims 13 to 16 wherein the ratio of Initiator is between 3:1 and 1:100.

19. The use of catalyst according to ~~claims 13 to 16~~ <sup>claim 13</sup>, where the polymerisation is undertaken in water, a protic or non-protic solvent.

20. The use of a catalyst according to ~~claims 1 to 12~~ <sup>claim 1</sup> to produce a statistical copolymer, a block copolymer, a telechelic polymer or a comb and graft copolymer of monomers according to previous claim.

add B6